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FABRICATION OF THIN LAYER BETA ALUMINA

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ABSTRACT

Beta"-alumina tubes having walls 700 μm , 300 μm , and 140 μm were processed by extrusion and sintering utilizing Ford proprietary binder and fabrication systems. Tubes prepared by this method have properties similar to tubes prepared by isostatic pressing and sintering, i.e. density greater than 98% of theoretical, resistivity $\sim 5 \Omega\text{cm}$ at 300°C and a helium leak rate less than $3 \times 10^{-9} \text{ cc/cm}^2/\text{sec}$.

Ford-developed ultrasonic bonding techniques were used for bonding β'' -alumina end caps to open ended β'' -alumina tubes prior to sintering. After sintering the bond is hermetic and the integrity of the bonded area is comparable to the body of the tube.

The following β'' -alumina membranes were sent to NASA:

- Four tubes 6 mm O.D., 300 μm wall, closed at one end with glass, sealed to α -alumina.
- Two end-capped tubes, 10 mm O.D., 700 μm wall, sealed to α -alumina.

SUMMARY

In April of 1976 the Ford Motor Company entered into a contract with NASA and agreed to perform the following task under Contract NAS-19782: The Contractor shall perform the work described hereinafter. At the end of the contract period, no less than two and no more than four tubes shall be sent to the project manager. The samples shall have the following characteristics:

1. Tubes shall be approximately 2.5 cm long, with inside diameters of approximately 6 mm and a wall thickness not exceeding 150 microns.
2. Membranes shall have densities greater than 97% to assure good hermeticity. Such densities have generally resulted in strengths above 15,000 psi in the past.
3. Membranes shall have resistance less than $0.5 \Omega \text{ cm}^2$ at 300°C which is equivalent to $1.8 \Omega \text{ cm}^2$ at 150°C .
4. Membranes shall consist primarily of $\epsilon\text{-Al}_2\text{O}_3$. However, minority phases such as $\beta\text{-Al}_2\text{O}_3$ may be present.

After periods of approximately 3, 6 and 9 months from the date of this contract, one $\epsilon\text{-Al}_2\text{O}_3$ tube shall be delivered to the NASA Project Manager. The sample shall be representative of our most advanced state of the extrusion processing at that time.

This contract was later amended in the following manner:

The Contractor shall perform the work described hereinafter. At the end of the contract period, no less than four and no more than eight sealed tubes shall be delivered to the Project Manager. The samples shall have the following characteristics:

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- a. Tubes shall be approximately 6.6 cm long with inside diameters of approximately 6 mm or 10 mm and a wall thickness not exceeding 300 or 700 microns, respectively.
- b. First using the 300 micron tubing, the Contractor shall develop a method of sealing one end of the tubing to enable the tubes to hold molten sodium. If the 300 micron tubing cannot be sealed, the Contractor shall develop a sealing method for the 700 micron tubing.
- c. The open ends of the tubing successfully sealed to hold molten sodium shall be sealed to an insulating header.
- d. The sealed tubing shall be characterized as in Task I, Paragraphs 2, 3 and 4.

Proprietary binder systems have been developed at Ford for use in preparing ceramic automotive exhaust catalyst supports and turbine re-generator cores. Modifications of these binder systems were used in preliminary studies of the extrusion of β "-alumina tubes having diameters >10 mm and wall thicknesses >1 mm. Therefore, it was decided to further modify the processing conditions in an attempt to prepare thin-walled membranes. A successful program would not only result in a technique for the preparation of thin membranes for use in devices such as low-temperature Na-S batteries, but would aid in the development of a useful ceramic processing method. As a result of the successful modification of a binder system, an extrusion process and a sintering process, β "-alumina tubes having walls 700 μ m, 300 μ m and 140 μ m were prepared. These tubes were found to have properties similar to tubes prepared by isostatic pressing and sintering, i.e. density greater than 98% of theoretical, resistivity $\sim 5 \Omega\text{cm}$ at 300°C and a helium leak rate less than $3 \times 10^{-9} \text{ cc/cm}^2/\text{sec}$.

Ford-developed ultrasonic bonding techniques were used for bonding β'' -alumina end caps to open ended β'' -alumina tubes prior to sintering. After sintering the bond was found to be hermetic and its integrity was comparable to the body of the tube.

The following β'' -alumina membranes were sent to NASA in fulfillment of contract objectives:

- One tube, 10 mm O.D., 700 μ m wall, open ended
- One tube, 6 mm O.D., 300 μ m wall, open ended
- One tube, 6 mm O.D., 140 μ m wall, open ended
- Four tubes, 6 mm O.D., 300 μ m wall, closed at one end with glass, sealed to α -alumina.
- Two end-capped tubes, 10 mm O.D., 700 μ m wall, sealed to α -alumina.

INTRODUCTION

In response to NASA RFP No. 3-573275Q, the Ford Motor Company submitted a proposal to fabricate thin β -alumina membranes. This program was a logical extension of prior work done at Ford on the fabrication of β'' -alumina membranes and on the preparation of thin-walled ceramic bodies by the extrusion of polymer-ceramic composites.

The Ford Motor Company has been involved in the study of β - Al_2O_3 and related materials for over ten years* (1-24, 30-45). From early fundamental studies of ionic diffusion to current research and development projects involving Na-S battery and sodium thermo-electric generators, the main thrust of the investigations has been directed toward the preparation of ceramic membranes. Research in this area has been successful, resulting in many patents and publications. A wealth of information has been accumulated on the shaping, processing, and sealing of β'' - Al_2O_3 as well as the effects of processing parameters and composition on the sintered materials.

Early attempts to prepare β - Al_2O_3 membranes for use in Na-S batteries indicated that β'' -alumina had conductivity superior to β - Al_2O_3 , but could not be sintered readily because of decomposition near the sintering temperature. When small amounts of stabilizers such as Li_2O or MgO were added, the thermal stability of the β'' -alumina was increased so that it could be sintered without decomposition.

Ceramic materials were then developed which could be sintered into membranes having adequate strength, conductivity and resistance to chemical corrosion. However, when the membranes were subjected to the passage of high

*In this discussion the term β'' - Al_2O_3 will be used to refer to materials which are primarily β'' - Al_2O_3 but may also contain small amounts of other materials such as β - Al_2O_3 , Na_2O , Al_2O_3 and Li_2O Al_2O_3 .

sodium-ion currents under certain electrolytic conditions, they developed cracks. This phenomenon was found to be a function of β'' -alumina ceramic composition. A mechanism of ceramic degradation has been proposed²¹ and a series of compositions in the $\text{Na}_2\text{O} - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3$ system has been developed and fabricated into membranes capable of passing high currents without degradation.²³

Techniques have been developed for the preparation of β'' -alumina membranes having specific configurations for use in various electrochemical devices. For example, tubes 1 cm OD, 0.8 cm ID and 14 cm long were routinely prepared by mixing Na_2CO_3 , LiNO_3 , and $\alpha - \text{Al}_2\text{O}_3$ together in the proper ratios, calcining at $800^\circ\text{C} - 1250^\circ\text{C}$ and milling to break down agglomerates. The powder was then mixed with a binder, and isostatically pressed in a tubular mold at 55,000 psi. After the binder was burned off, the tubes were encapsulated in platinum containers and sintered at $1500^\circ\text{C} - 1600^\circ\text{C}$.

However, this method is not well suited to the preparation of tubes having walls less than 0.7 mm thick. There are formidable problems associated with mold filling prior to isostatic pressing and sample removal after pressing.

Techniques have also been developed for sealing β'' -alumina membranes to construction materials such as alumina using appropriate sealing glasses. Such seals have proved to be stable over long periods of time at elevated temperatures in the presence of sodium, sulfur, and sodium polysulfide. Such seals also may be used for closing open-ended tubes.

Ford has also been involved for many years in the preparation of polymers highly loaded with metallic and ceramic fillers. Thermally-conducting

rubber composites have been prepared containing 58% by volume of various metal fillers, and polymer composites containing 50% by volume of SiC have been injection molded. These moldings are used in the preparation of reaction-sintered SiC turbine components.

Proprietary binder systems have been developed at Ford for use in preparing ceramic automotive exhaust catalyst supports and turbine regenerator cores from thin ribbed sheets 170 μ m thick containing 60% cordierite ($\text{Mg}_2 \text{Al}_4 \text{Si}_5 \text{O}_{18}$) by volume. The flexible sheets are prepared by calendering and embossing and then are wound into a complex shape and sintered. In addition, honeycomb shaped structures have been extruded containing 60% cordierite by volume.

Modifications of these binder systems were used in preliminary studies of the extrusion of β "-alumina tubes having diameters >10 mm and wall thicknesses >1 mm. Therefore, it was decided to further modify the processing conditions in an attempt to prepare thin-walled membranes. A successful program would not only result in a technique for the preparation of thin membranes for use in devices such as low-temperature Na-S batteries, but would aid in the development of a useful ceramic processing method.

As a result of the proposal Ford entered into a contract with NASA and agreed to perform the following task under contract NAS3-19782:

Task I - The Contractor shall perform the work described hereinafter. At the end of the contract period, no less than two and no more than four tubes shall be sent to the project manager. The samples shall have the following characteristics:

1. Tubes shall be approximately 2.5 cm long, with inside diameters of approximately 6 mm and a wall thickness not exceeding 150 microns.
2. Membranes shall have densities greater than 97% to assure good hermeticity. Such densities have generally resulted in strengths above 15,000 psi in the past.

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3. Membranes shall have resistances less than $0.5 \Omega \text{ cm}^2$ at 300°C which is equivalent to $1.8 \Omega \text{ cm}^2$ at 150°C .
4. Membranes shall consist primarily of $\beta''\text{-Al}_2\text{O}_3$. However, minority phases such as $\beta\text{-Al}_2\text{O}_3$ may be present.

After periods of approximately 3, 6, and 9 months from the date of this contract, one $\beta''\text{-Al}_2\text{O}_3$ tube shall be delivered to the NASA Project Manager. The sample shall be representative of our most advanced state of the extrusion processing at that time.

This contract was later amended in the following manner:

The Contractor shall perform the work described hereinafter. At the end of the contract period, no less than four and no more than eight sealed tubes shall be delivered to the Project Manager. The samples shall have the following characteristics:

- a. Tubes shall be approximately 6.6 cm long with inside diameters of approximately 6 mm or 10 mm and a wall thickness not exceeding 300 or 700 microns, respectively.
- b. First using the 300 micron tubing, the Contractor shall develop a method of sealing one end of the tubing to enable the tubes to hold molten sodium. If the 300 micron tubing cannot be sealed, the Contractor shall develop a sealing method for the 700 micron tubing.
- c. The open ends of the tubing successfully sealed to hold molten sodium shall be sealed to an insulating header.
- d. The sealed tubing shall be characterized as in Task I, Paragraphs 2, 3, and 4.

EXPERIMENTAL

The fabrication of thin walled β'' -alumina tubes requires the following operations:

- a. The preparation of a powdered β'' -alumina precursor.
- b. Mixing the powder with the binder ingredients.
- c. Extrusion of the tubes.
- d. End capping of the tubes.
- e. Burning off the binder.
- f. Sintering the green tubes.
- g. Characterization of the sintered tubes.

The end-capping procedure can either be performed in the green state by techniques described later or performed on the sintered β'' -alumina tube by glass sealing. Both of these techniques have been used. The binder system and mixing procedures used in fulfilling this contract are the proprietary ones developed by Ford prior to contract NAS3-19782 and will not be described further. The extrusion procedures and end-capping techniques pursued under contract NAS3-19782 are described below.

a) The preparation of a powdered β'' -alumina precursor: Dried samples of Na_2CO_3 and LiNO_3 were mixed with Linde C Al_2O_3 and milled for one hour in a polyethylene container using high-purity Al_2O_3 balls. The ratio of reagents was chosen so that the final products would have compositions of 8.7% Na_2O - 0.7% Li_2O - 90.6% Al_2O_3 , 8.85% Na_2O - 0.75% Li_2O - 90.4% Li_2O , and 9.0% Na_2O - 0.8% Li_2O - 90.2% Al_2O_3 . The powders were calcined for two hours at 1260°C in platinum crucibles. On cooling the powders were crushed and milled for one hour in polyethylene vessels using Al_2O_3 balls.

b) Mixing the powder with the binder ingredients: Both the binder ingredients and the mixing procedure are proprietary.

c) Extrusion: A ram type extrusion apparatus (Figures 1,2,) was used to extrude the green body tubes (Figure 4). Two sizes of tubes were extruded (approximately 12 mm diameter with 1000 μm wall and approximately 7 mm diameter with 400 μm wall.* The techniques for extruding these sizes differed primarily in the die set used for the extrusion (Figure 3). Therefore it may be assumed that intermediate sizes can also be prepared.

To perform the extrusion, mixed binder and ceramic composition is broken or cut into a size convenient for insertion into the barrel of the extruder. After insertion into the preheated extruder barrel, the ram is inserted and a force of approximately 250 kg to 500 kg is applied to pack

* During binder burn out and sintering tubes shrink by ~20%.

the composition. At this point the ram is stopped and the force allowed to decay as the composition is preheated for about 15 minutes prior to extrusion. After the preheat, the ram is once again forced against the composition until tube extrudes from the die orifice. The rate at which tube is extruded and the temperatures of the barrel and die are adjusted until a smooth tube is obtained. Typical extrusion rates are 600 mm/min for the 12 mm tube and 100 mm/min for the 7 mm tube. The tube is extruded over a mandrel of 10.5 mm diameter for the 12 mm tubing and 6.5 mm diameter for the 7 mm tubing. This is done to maintain straight tubing while the green body is still hot enough to deform easily. After a sufficient length of tubing has been extruded, it is cut from the die and placed on another mandrel for cooling to room temperature. After reaching ambient temperature, the tubing can be easily handled, cut and stored without use of a mandrel.

d) End-Capping: End-capping in the green state can be performed in several ways. The end-caps may be solvent bonded, bonded with a mixture of binder/ceramic composition in a solvent or ultrasonically bonded. All of these techniques have been explored and will be described below. However, ultrasonic bonding appears to have the most promise.

The end-caps are cut from composition milled to a thickness suitable for the particular wall thickness of the tube being end-capped. The hot milling is the final phase of the mixing procedure. Although several thicknesses of end-caps have been explored, we have found that a thickness of 1 mm for the 12 mm diameter tube and 0.5 mm for the 7 mm diameter tube are more suitable. Both flat and hemispherically shaped end-caps have been explored. A better success rate in obtaining crack-free end-caps after

sintering has been obtained with the hemispherically shaped end-caps. The hemispherically shaped end-caps were obtained by taking discs cut from milled sheet and pressing these discs into a hemispherical teflon cavity (heated to 150°C) using a brass or steel mandrel whose end has been shaped to give the desired hemispherical shape of the interior of the end-cap (Figure 4).

When solvent bonding, the tube end is dipped into a suitable solvent such as methyl ethyl ketone. The end-cap and tube are then brought together and additional solvent is used in small quantities to smooth the interface.

When using an adhesive composed of a portion of the binder/ceramic mixed in methyl ethyl ketone, the procedure for solvent bonding is also followed with the adhesive being substituted for the solvent. Small quantities of the solvent may be used for final smoothing of the interface.

The apparatus for ultrasonic bonding is shown in Figure 5. A tube which has been carefully cut to give a smooth surface whose face is perpendicular to the length of the tube is placed over a mandrel. The horn of the ultrasonic welder (Branson, Model 400C, ultrasonic welder) has a tube shape with a hemispherical end cut into the base of the horn. The end-cap is placed up into the horn and positioned with a solid rod having a flat end cut perpendicular to the length of the rod. The horn of the ultrasonic welder is then carefully brought down to give initial contact between the end-cap and the tube. Ultrasonic power is applied while the horn is lowered to its final position to produce the bond. Although not mandatory, a better success rate in producing helium leak tight end-capped tubes (Figure 6) was achieved if the tubes were rotated during the ultrasonic bonding and if the

edge of the end-cap was shaped so that it would be parallel to the edge of the tube to which it is to be bonded. Generally, a total time of 15 seconds from power on to power off was adequate. After the power was turned off, the horn was allowed to remain in contact with the tube for another 5 to 15 seconds and then raised to allow removal of the tube from the mandrel.

e) Binder Removal: Binder removal is accomplished by heating the tubes in a circulating oven (Temperite, Type MU 182424A) using filtered air as the atmosphere. Several temperature programs have been used during this contract period. However, no attempt has been made to minimize the time of the burn-out schedule. It has been found to be advantageous to support the tubes in a vertical position by slipping them over an alumina mandrel whose diameter is small enough to allow for shrinkage of the tube during binder removal. The tubes were removed from the burn-out oven and placed immediately in a desiccator which has been preheated to 65°C. Tubes and desiccator are allowed to cool to room temperature and the tubes are held in the desiccator until needed for sintering.

f) Sintering: After binder burn out tubes were encapsulated in platinum cylinders and arranged in vertical positions in a cold furnace. The furnace was slowly heated to 1585°C, held for fifteen minutes, cooled to 1400°C, held for one hour, then allowed to cool to room temperature.

The sintered β -Al₂O₃ tubes were sealed to α -Al₂O₃ substrates and some of the tubes were end capped with glass. Both techniques involved proprietary processes developed at Ford prior to this project and will not be described further.

g) Characterization: Both powders and sintered samples were examined by X-ray diffraction to determine phase distribution. Particle size distribution was determined by Coulter Counter analysis and Scanning Electron Microscopy. Density of the sintered samples was measured by the

method of Archimedes using methanol. Hermiticity of the tubes was determined with a Veeco Model 12 helium leak detector. Membrane resistivity was determined by two methods: A.C. measurements were made with a Wayne Kerr universal bridge, Model 3221 at 1592 Hz. using molten NaNO_2 - NaNO_3 contacts, D.C. measurements were made using molten sodium contacts as shown in Fig. 10. Modulus of rupture was determined by breaking ring shaped segments of tubes on an Instron testing machine.

RESULTS AND OBSERVATIONS

a) Preparation of Powdered β'' -alumina Precursors: Three compositions of β'' -alumina precursor powders were investigated. It was found that each composition could be fabricated, with minor processing variations, into membranes having satisfactory properties. Since the preferred composition of the β'' -alumina membrane used in the Ford Sodium Sulfur Battery is 8.85% Na_2O - 0.75% Li_2O - 90.4% Al_2O_3 , that composition was also used in most of the studies described in this report. X-ray diffraction indicated that the powders were primarily β - Al_2O_3 and Na_2O - Al_2O_3 with smaller amounts of β'' -alumina and traces of α - Al_2O_3 . Scanning Electron Microscopy indicated that the milling operation effectively broke down the loosely bonded agglomerates formed during calcination leaving irregularly shaped porous particles. The following is a typical particle size distribution:

<u>Particle Diameter (in microns)</u>	<u>Particle Distribution</u>
< 1.5	22%
1.5 - 2	8%
2 - 3	10%
3 - 4	8%
4 - 5	9%
5 - 6	4%
6 - 8	5%
8 - 10	6%
10 - 13	6%
13 - 15	5%
15 - 20	5%
> 20	12%

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b) Extrusion: The ability to extrude suitable tubes from a mixture of the Ford proprietary binder system with the precursor to β "-alumina is dependent on several factors among which are 1) time between mixing and extrusion, 2) geometry of the extrusion die, 3) temperature at which the extrusion is performed, 4) residence time in the barrel, 5) apparent viscosity of the mixture, and 6) the number of times the material has been extruded.

There appears to be an aging phenomenon in which more force is required to process the mixture and the quality of the extrudate deteriorates as a function of time after mixing. For the binder composition used, it is preferable to extrude the tubing within three days after mixing. Subsequent processing such as end-capping should also be done as soon after extrusion of the tubing as is practical with no more than two weeks elapsing.

In the extrusion die, the ratio of the length of the final tube section to the wall thickness of the tube being extruded is critical. Since the central mandrel requires three positioning screws (Figure 3) to maintain the mandrel in a centered position in the die, the material must have sufficient length of life for the strips produced at the centering screws to "knit" into a smooth, sound tube. Too short a die will result in extrusion of strips of material while too long a die will require an excessive pressure to perform the extrusion. We have found a ratio of twelve suitable for use with the 12 mm tubes and a ratio of 61 suitable for use with the 7 mm tube having a green wall thickness of 400 microns.

At extrusion temperatures, the "life" of the mixture in the barrel is approximately one hour. This will be slightly longer or shorter depending on the time that has elapsed since the material was mixed and the quality of tube needed.

The apparent viscosity of the material should be high enough to develop the back pressure needed for knitting of the strips to form a tube.

At too low an apparent viscosity, strips are extruded. Of course, if the viscosity is too high, excessive pressure will be required to perform the extrusion. Thus careful tailoring of the die and the mixture to be extruded is required for preparation of good tubing.

Although the mixture can be re-extruded, the quality of the extrudate suffers with each subsequent extrusion. A maximum of two extrusions was used in the preparation of the tubing.

c) End-Capping: Ultrasonic bonding produces the best bond for the 12 mm tube having a 1 mm wall thickness (Figures 7, 8). At this wall thickness, solvent bonding must be done very carefully or bubbling will result on burn-off of the binder. It is also very difficult to consistently bond tubes so that they have a uniform joint. Often some sections of the joint are very thin but are deceiving in that they will check helium leak tight (Figure 9). The 7 mm diameter tubes with the 400 micron (green state) wall thickness are difficult to bond ultrasonically because of the careful positioning of the end-cap relative to the tube which is required. In this case, glass sealing of the end-caps after sintering was the most successful. Careful control of the position of the end-cap relative to the tube is essential for both sizes of tubes. Rotation of the tubes during the sealing process was also found necessary to achieve an even leaktight seal. It becomes particularly difficult to do this with the 7 mm tubes. Support of the tube section was also needed for the 7 mm tube during application of the ultrasonics in order to be able to apply sufficient force during the bonding process. Ultrasonic bonding still holds promise for use with the 7 mm tube, but additional development is needed.

d) Binder Removal: The binder removal proceeded smoothly. Adequate air flow to carry away binder constituents during burn-off is important to prevent bubbling or cracks in the tubes. Because of the length of the tubes and the thin walls, it is desirable to burn-off in the vertical position using loose fitting mandrels to support the tubes and minimize deformation. It is also desirable to heat to a high enough temperature (i.e., 600°C) that the powder compact develops sufficient strength for handling prior to sintering. The binder is completely removed at 500°C, but the powder compact is friable with little strength. It is also subject to cracking from absorption of the small amount of moisture absorbed in handling and in storage in the desiccator. After heating to 600°C, the tubes are still weak but are strong enough to reach sintering intact.

e) Sintering: When sintering tubes having walls of 400 μm and 170 μm it was necessary to arrange them vertically to avoid elliptical distortion. During sintering the samples were encapsulated in platinum tubes in order to prevent the loss of Na_2O . This technique was effective in sintering tubes having walls 400 μm and 1000 μm thick. However, when membranes having 140 μm walls were sintered, enough Na_2O was lost from the small volume of the material in establishing an equilibrium vapor pressure within the platinum tube to prevent sintering to high densities. This problem was solved by placing partially sintered pellets of β'' -alumina in the platinum tubes with the thin membranes. Membranes having walls of 700 μm , 300 μm , and 140 μm were all sintered to densities greater than 98% of theoretical.

f) Characterization: Such tubes were hermetic, displaying He leak rates less than 3×10^{-9} cc/cm²/sec. X-ray diffraction indicated that the

materials consisted of β'' -alumina plus very small traces of β - Al_2O_3 . The resistivity and modulus of rupture of a typical tube 10 mm O.D. having walls 700 μm thick were 4.6 $\Omega\text{ cm}$ at 300°C and 500 MN/cm^2 . These tests were not carried out on tubes having thinner walls because the uncertainties inherent in both measurements increase with decreasing wall thickness. The purpose of the measurements on the 700 μm membranes was to demonstrate that the properties of the membranes formed by extrusion are comparable with the properties of membranes formed by the conventional method of isostatic pressing. It is particularly interesting to consider the end-caps ultrasonically bonded to the extruded tubes. No indication of an interface (Figure 8) could be detected by microscopic examination of cross sections cut from sintered bonds.

As a final test of membrane durability a β'' -alumina tube 30 mm long, having an O.D. of 6 mm and a wall thickness of 0.3 mm was prepared by extrusion and sintering. One end of the tube was closed with a sodium borosilicate glass and the other end was joined to an α - Al_2O_3 tube with glass. The tube was tested on a He leak detector and found to have a He leak rate $< 3 \times 10^{-9}$ $\text{ml/cm}^2/\text{sec}$.

This membrane was built into a device (Figure 10) which allowed the tube to be filled with sodium and immersed in a vessel full of sodium. A sodium-ion current could then be passed through the β'' -alumina membrane under the influence of an applied potential. Current densities up to 1000 Ma/cm^2 were passed through the membrane without damage at a temperature of 300°C. The resistivity of the membrane was $\sim 5 \Omega\text{ cm}$ ($0.15 \Omega\text{-cm}^2$) at 300°C and $\sim 24 \Omega\text{ cm}$ ($0.72 \Omega\text{-cm}^2$) at 150°C. The device was operated continuously at a current density of 500 Ma/cm^2 for a period of 30 days at a temperature of 300°C. At the end of that period there was no indication of damage.

CONCLUSION

A method has been developed for the the extrusion and sintering of thin walled β'' -alumina tubes (Fig. 11-15). A method has also been developed for the ultrasonic bonding of β'' -alumina end caps to tubes such that after sintering the bond is hermetic and the integrity of the bonded area is comparable to the body of the tube. In accordance with contract NAS 3-19782 the following specimens have been delivered to NASA, thereby fulfilling all contract requirements:

- a.) One β'' -alumina tube 25 mm long, 10 mm in diameter, 700 μ m wall.
- b.) One β'' -alumina tube, 25 mm long, 6 mm in diameter, 300 μ m wall.
- c.) One β'' -alumina tube, 25 mm long, 6 mm in diameter, 140 μ m wall.
- d.) Two β'' -alumina tubes, 76 mm long, 10 mm in diameter, 700 μ m wall, one end sealed with a β'' -alumina end cap, the open end sealed to an α -Al₂O₃ insulating header (Fig. 15).
- e.) Four β'' -alumina tubes, 76 mm long, 6 mm in diameter, 300 μ m wall, one end sealed with glass, the open end sealed to an α -Al₂O₃ insulating header.

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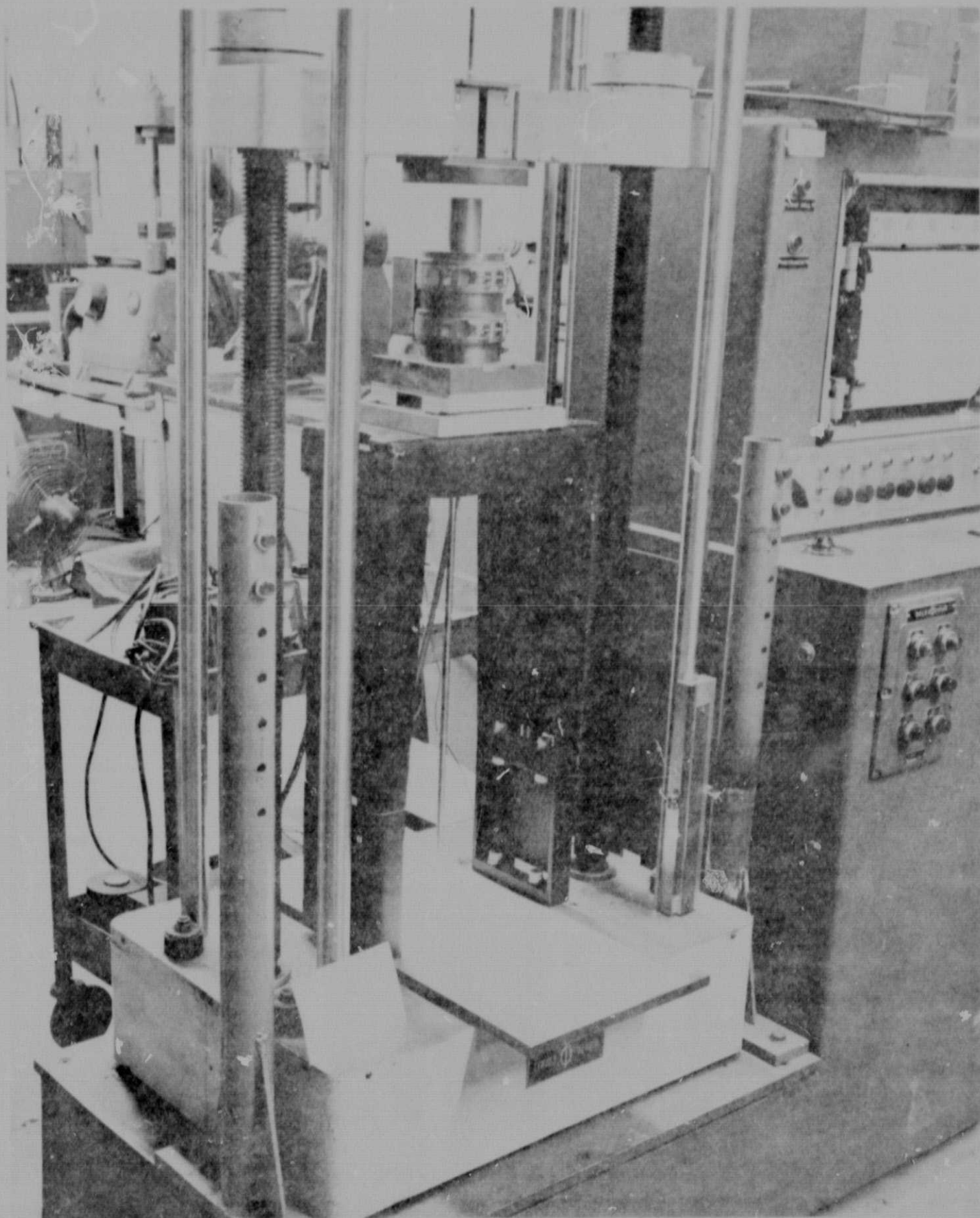


Fig. 1 Extrusion apparatus

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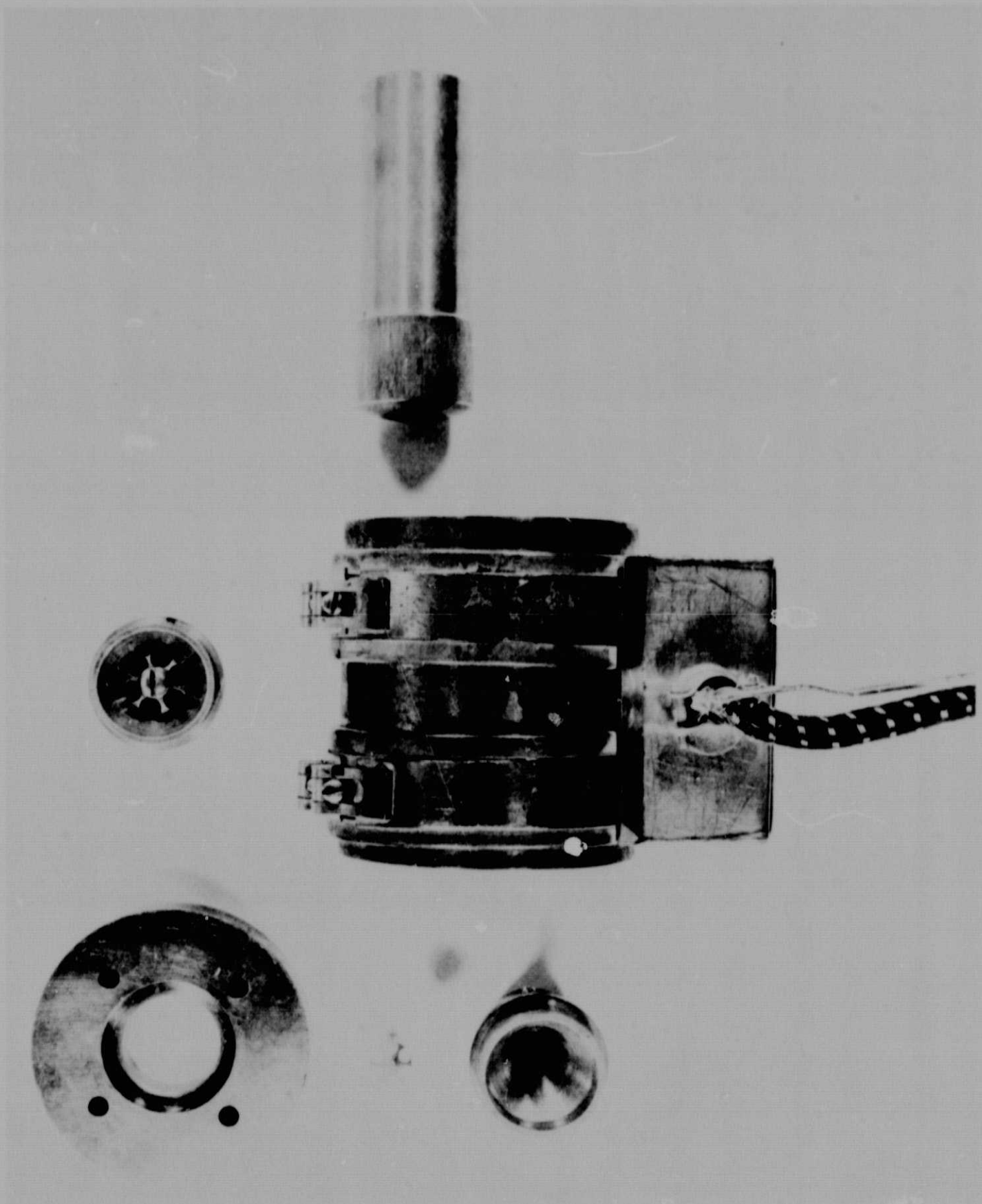


Fig. 2 Details of extrusion apparatus and die

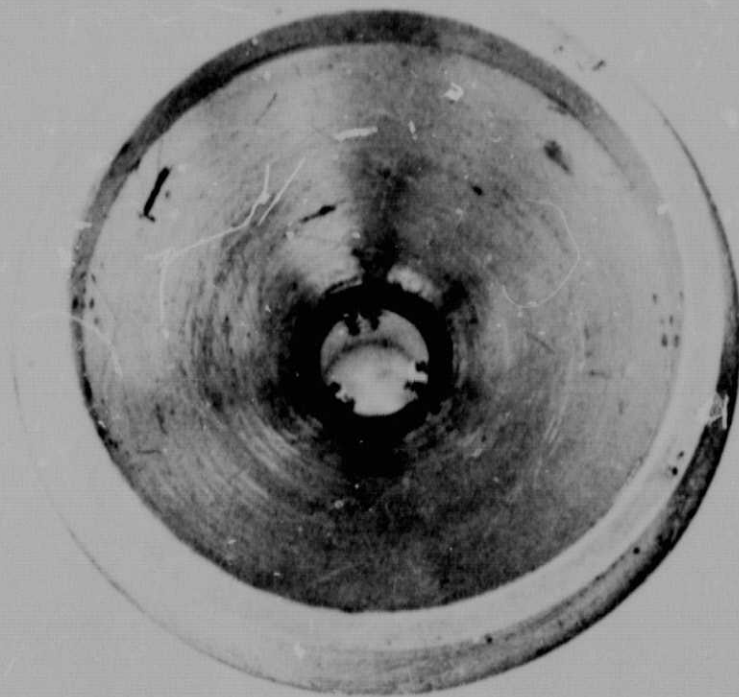


Fig. 3 Die for the extrusion of tubes, ~12 mm O.D.

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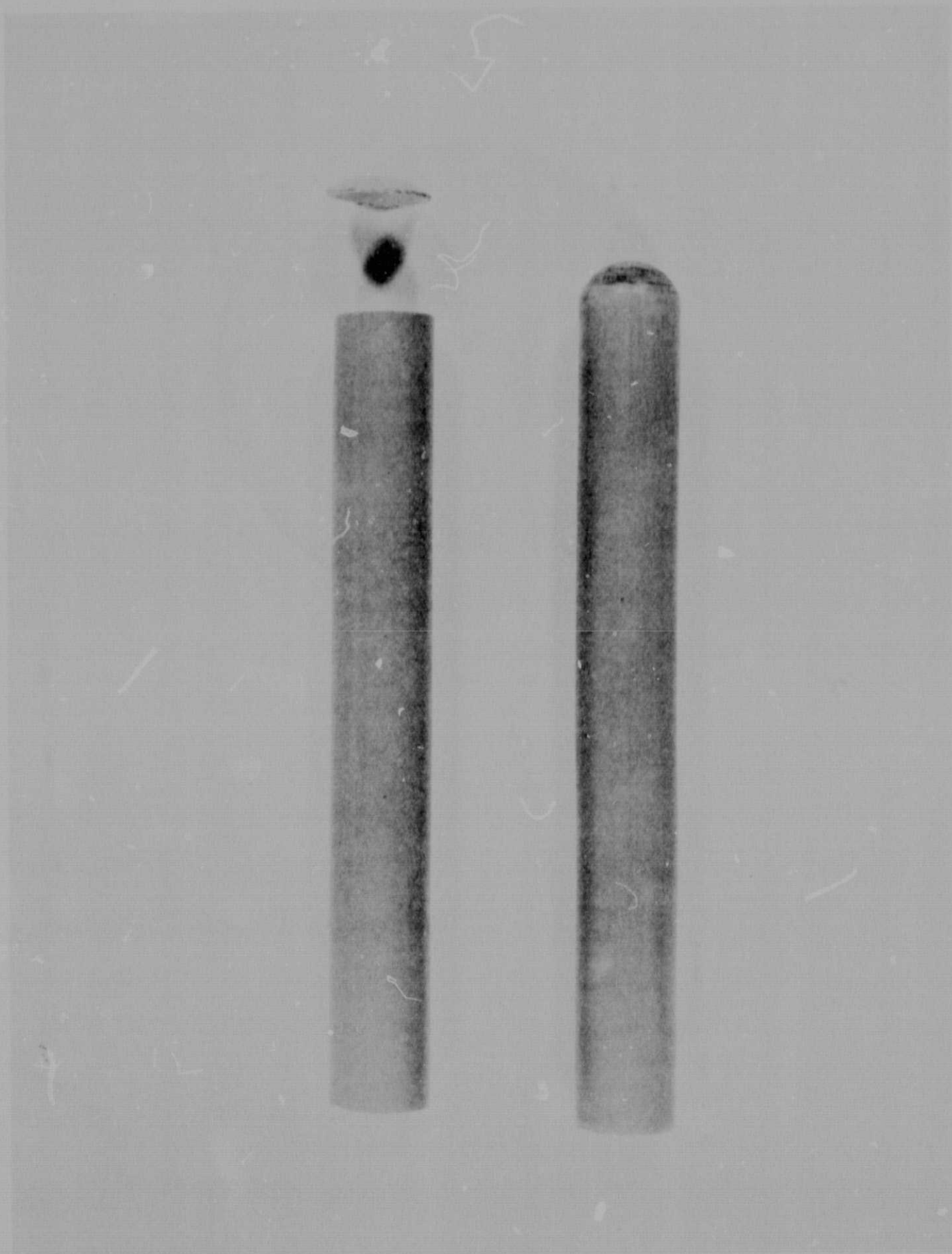
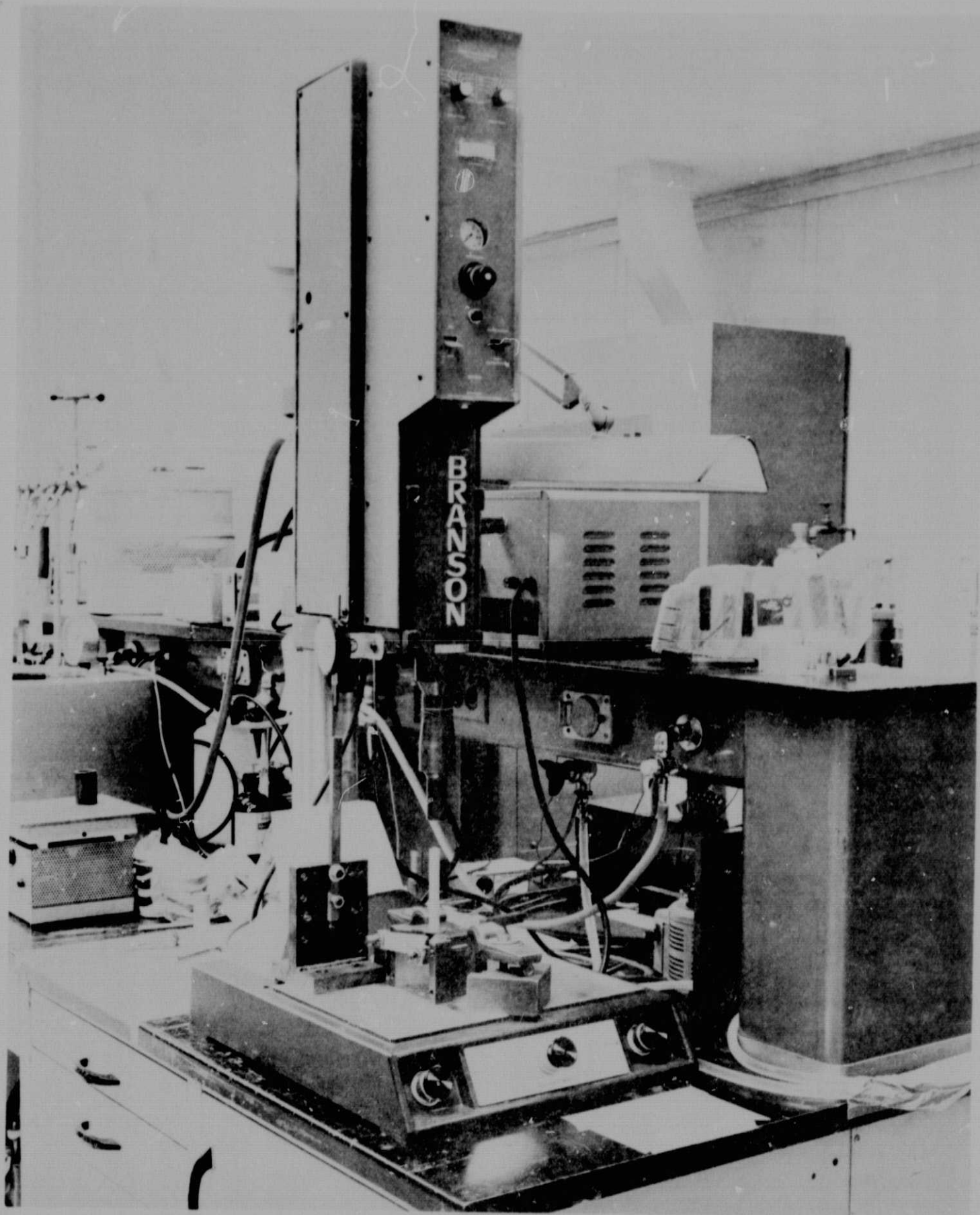


Fig. 4 Extruded tubes, ~12 mm O.D.



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Fig. 5 Apparatus for the ultrasonic sealing of tubes

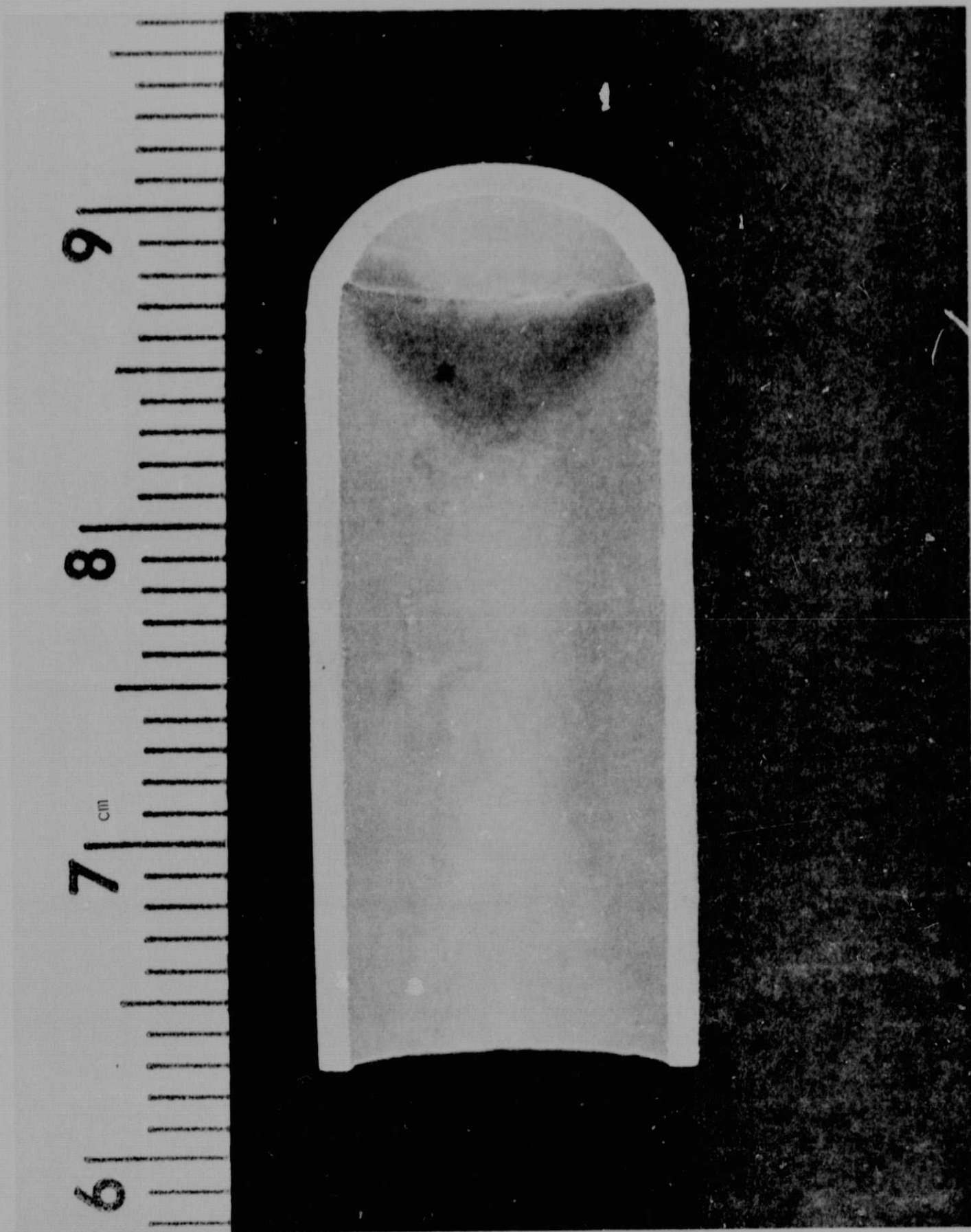


Fig. 6 Cross section of extruded, end-capped tube, ~ 12 mm O.D.

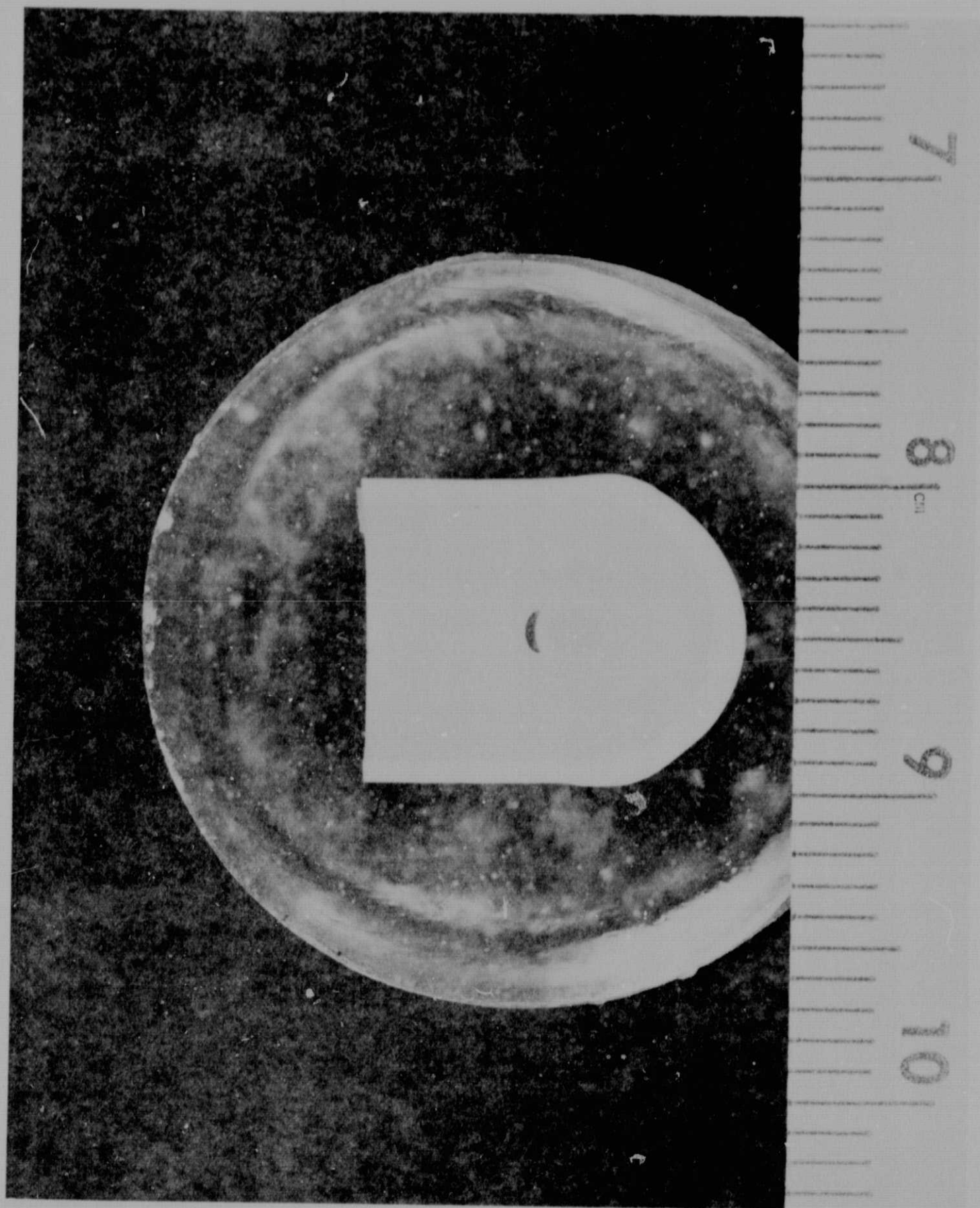


Fig. 7 Cross section of sintered, end-capped tube, 10 mm O.D.

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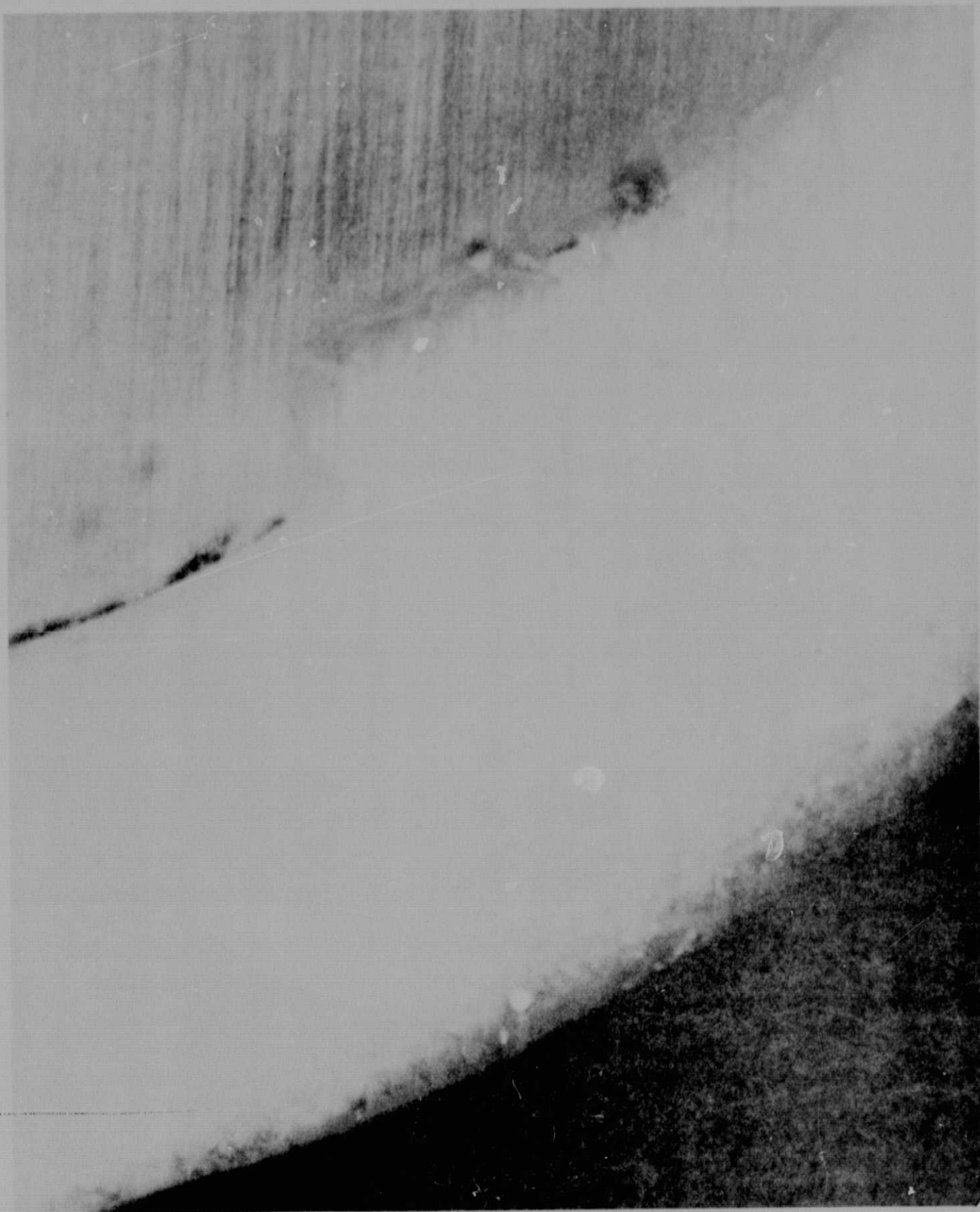


Fig. 8 Cross section of sintered, end-capped tube,
10 mm O.D. 150 X enlargement

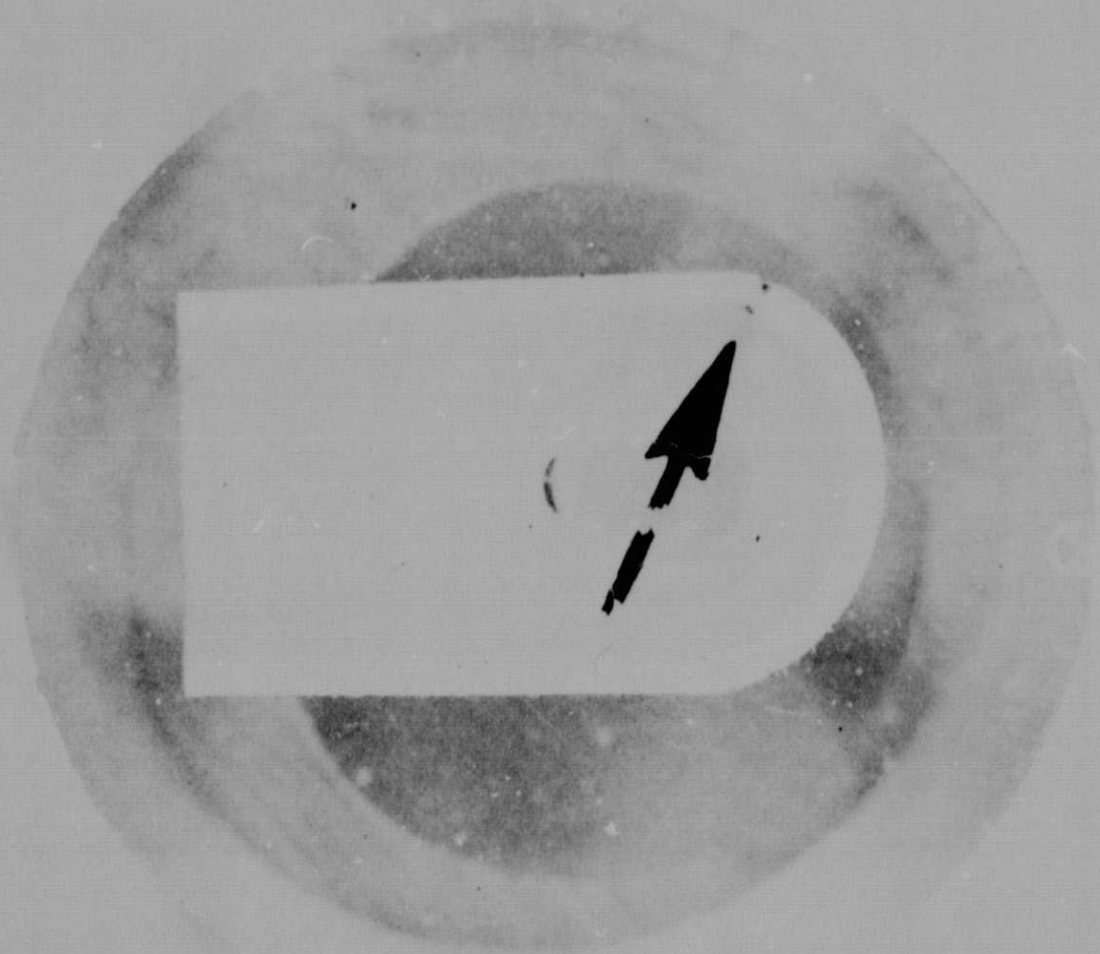


Fig. 9 Cross section of sintered end-capped tube,
10 mm O.D., having an imperfect bond

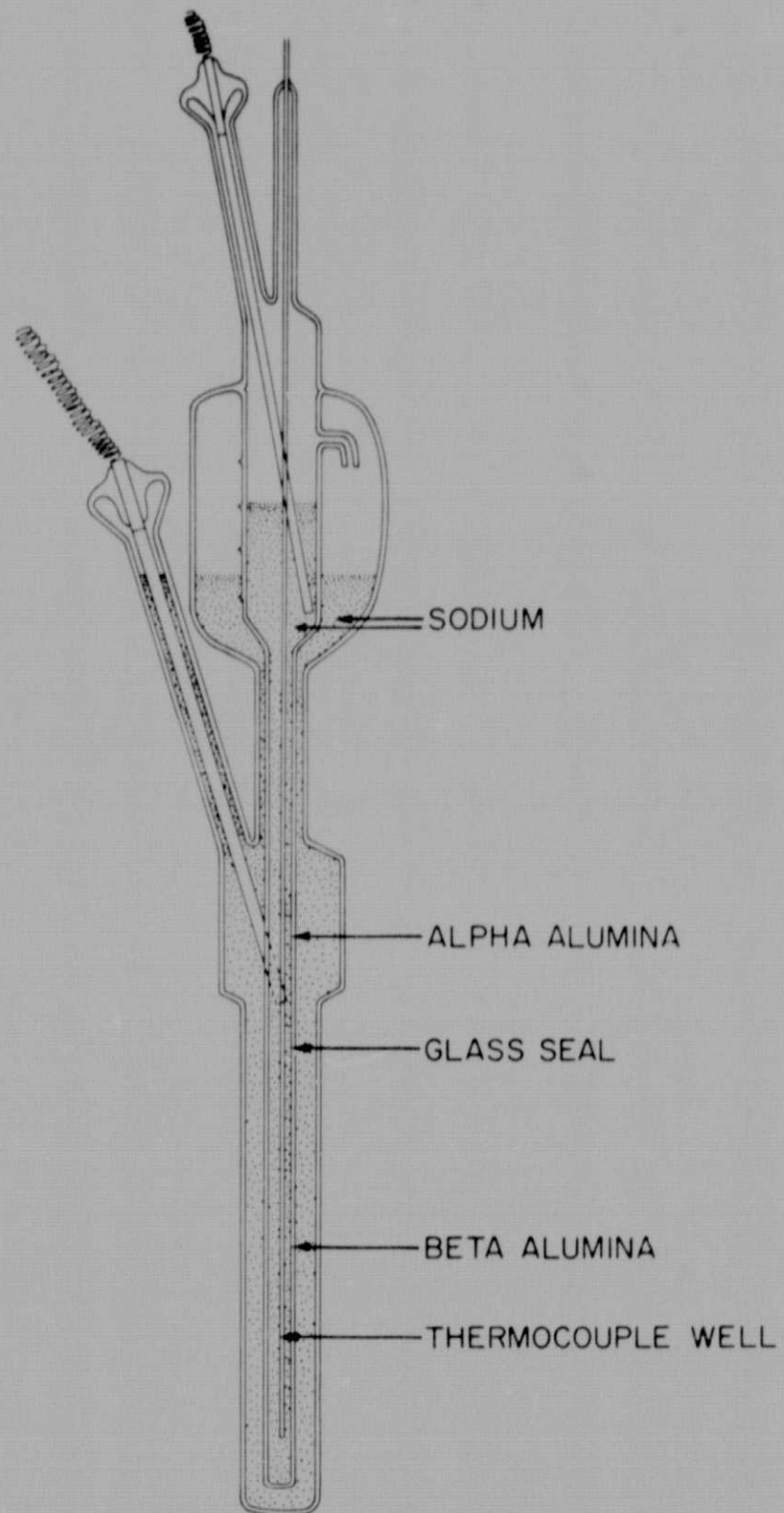


Fig. 10 Na-Na test cell

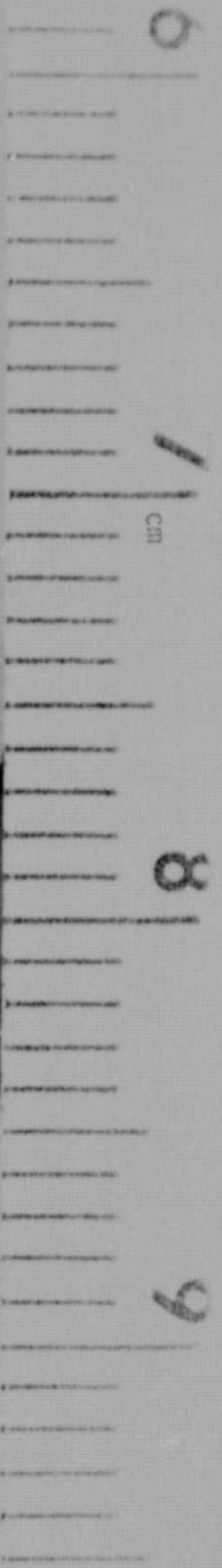
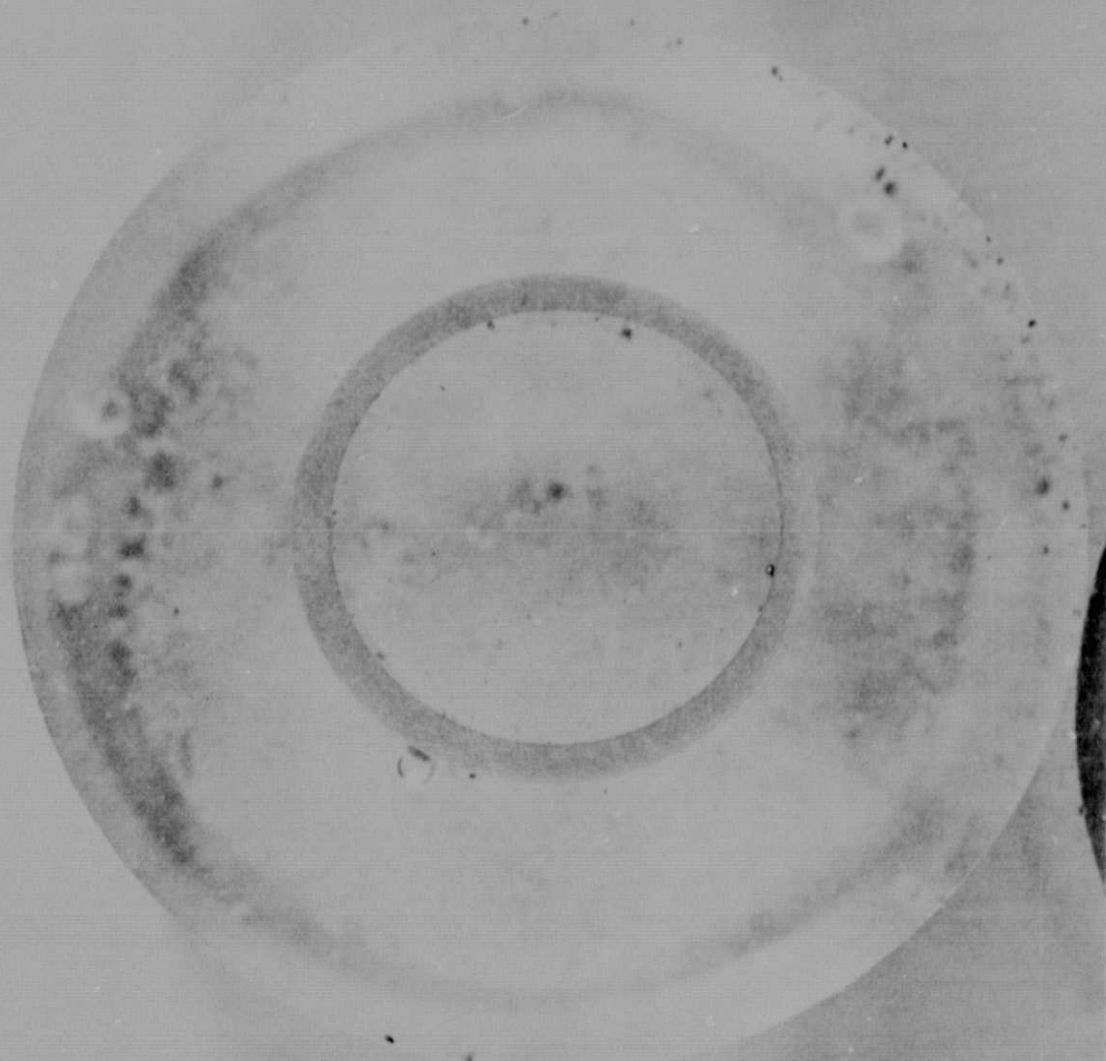


Fig. 11 Cross section of extruded tube ~12 mm O.D., having a wall ~1 mm thick

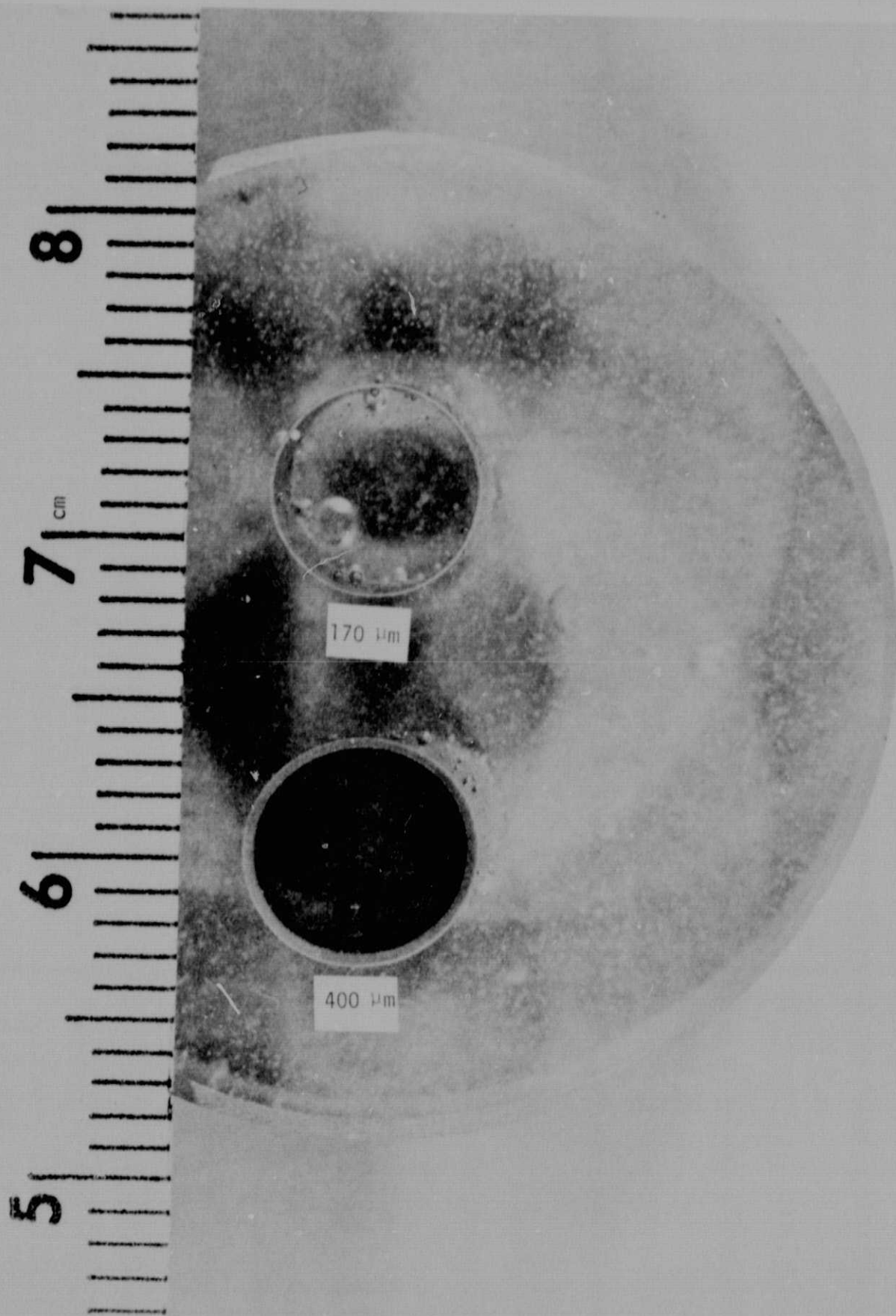


Fig. 12 Cross sections of extruded tubes ~7 mm O.D.,
having walls ~400 μm and ~170 μm thick

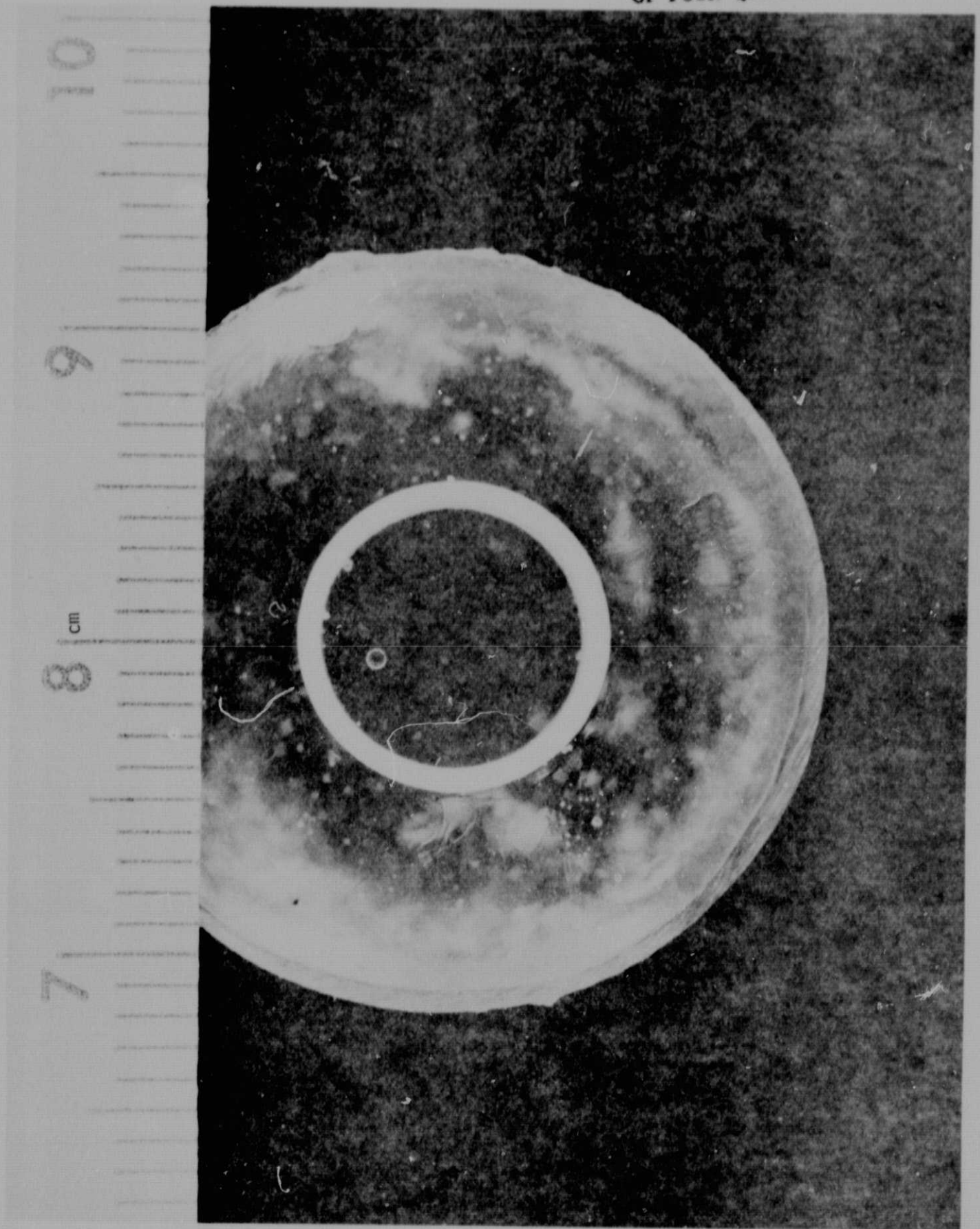


Fig. 13 Cross section of sintered tube, 10 mm O.D.,
having a wall $\sim 700 \mu\text{m}$ thick

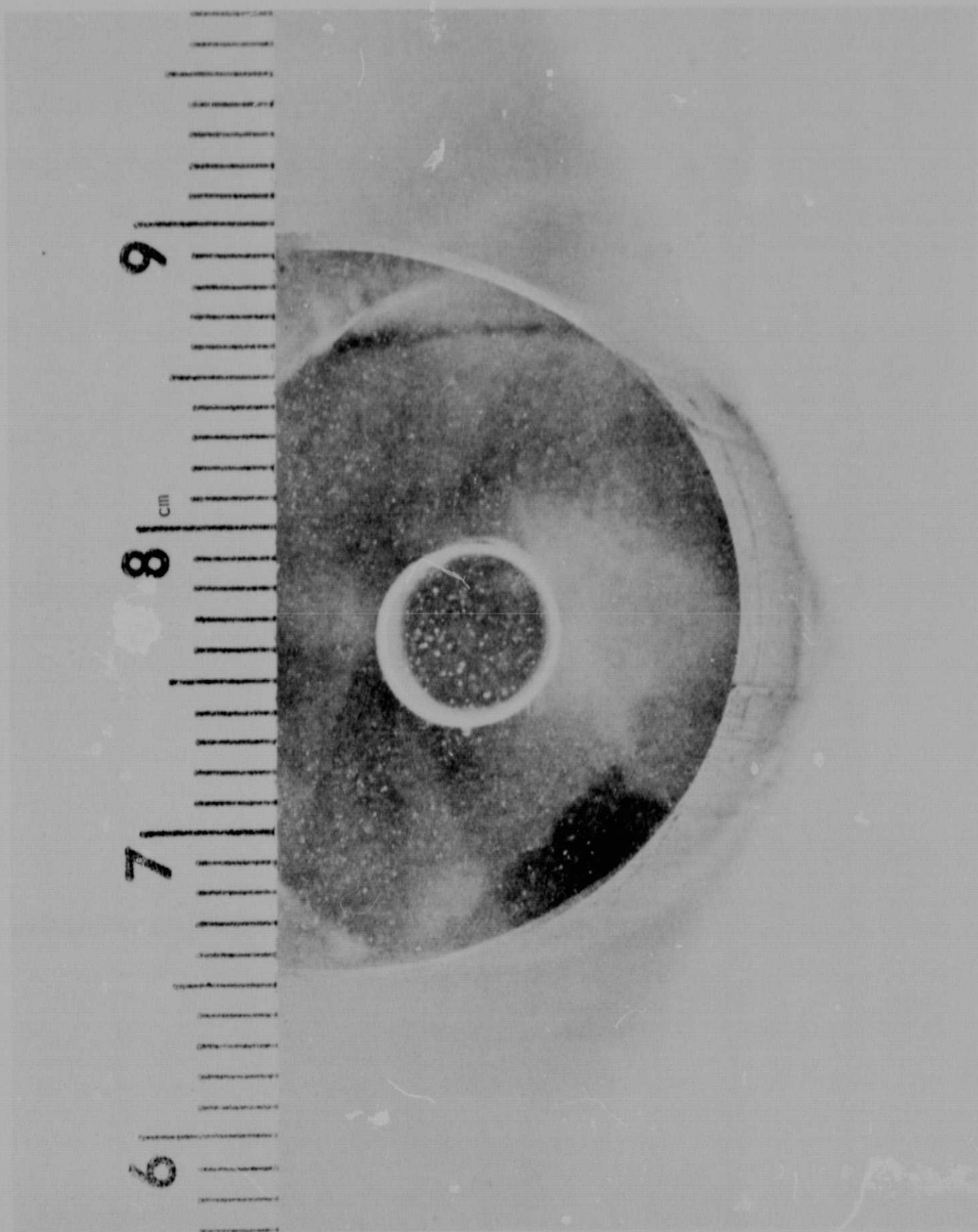


Fig. 14 Cross section of sintered tube, 6 mm O.D., having a wall 300 μ m thick

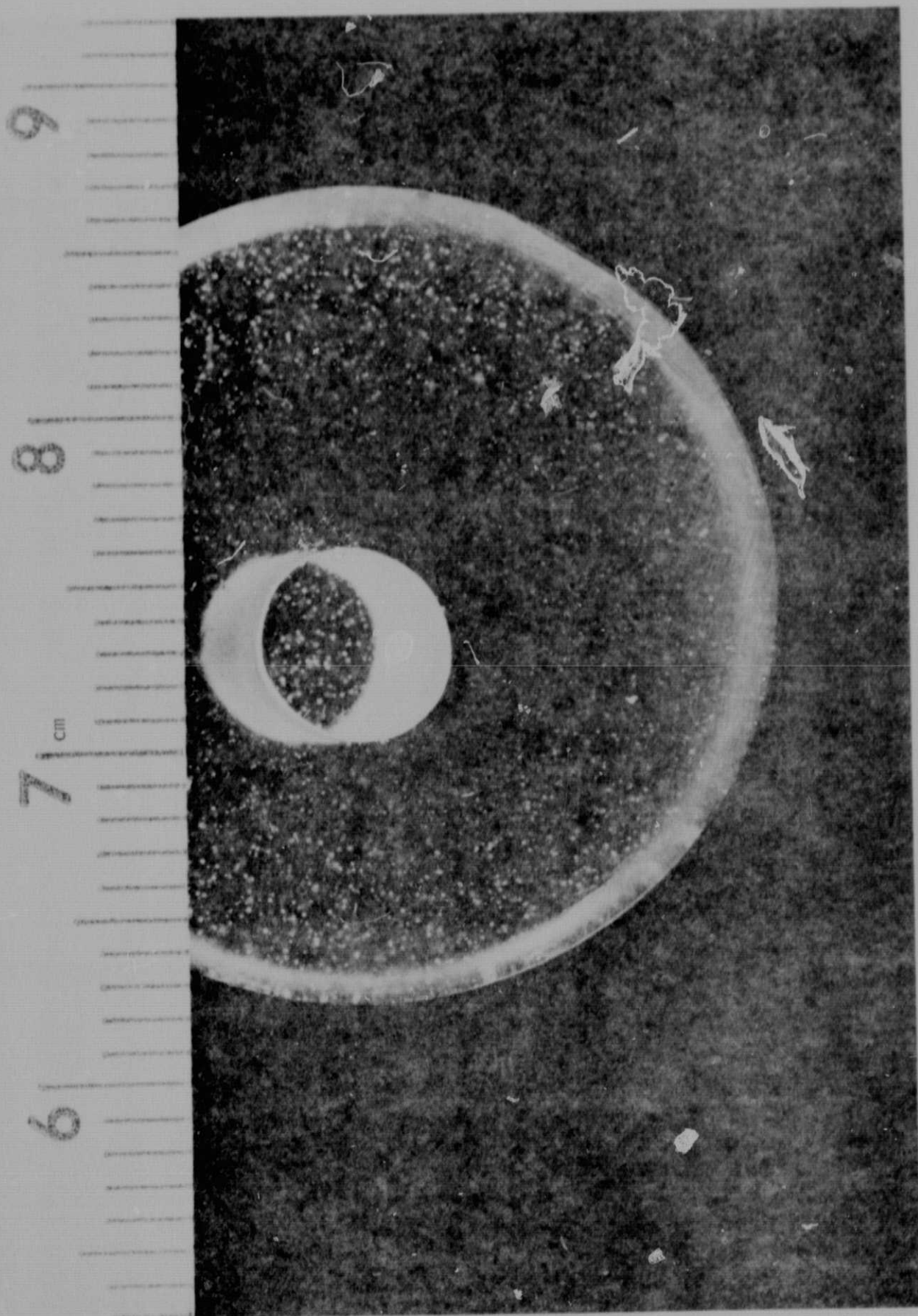


Fig. 15 Cross section of sintered tube, 6 mm O.D., having a wall 140 μ m thick

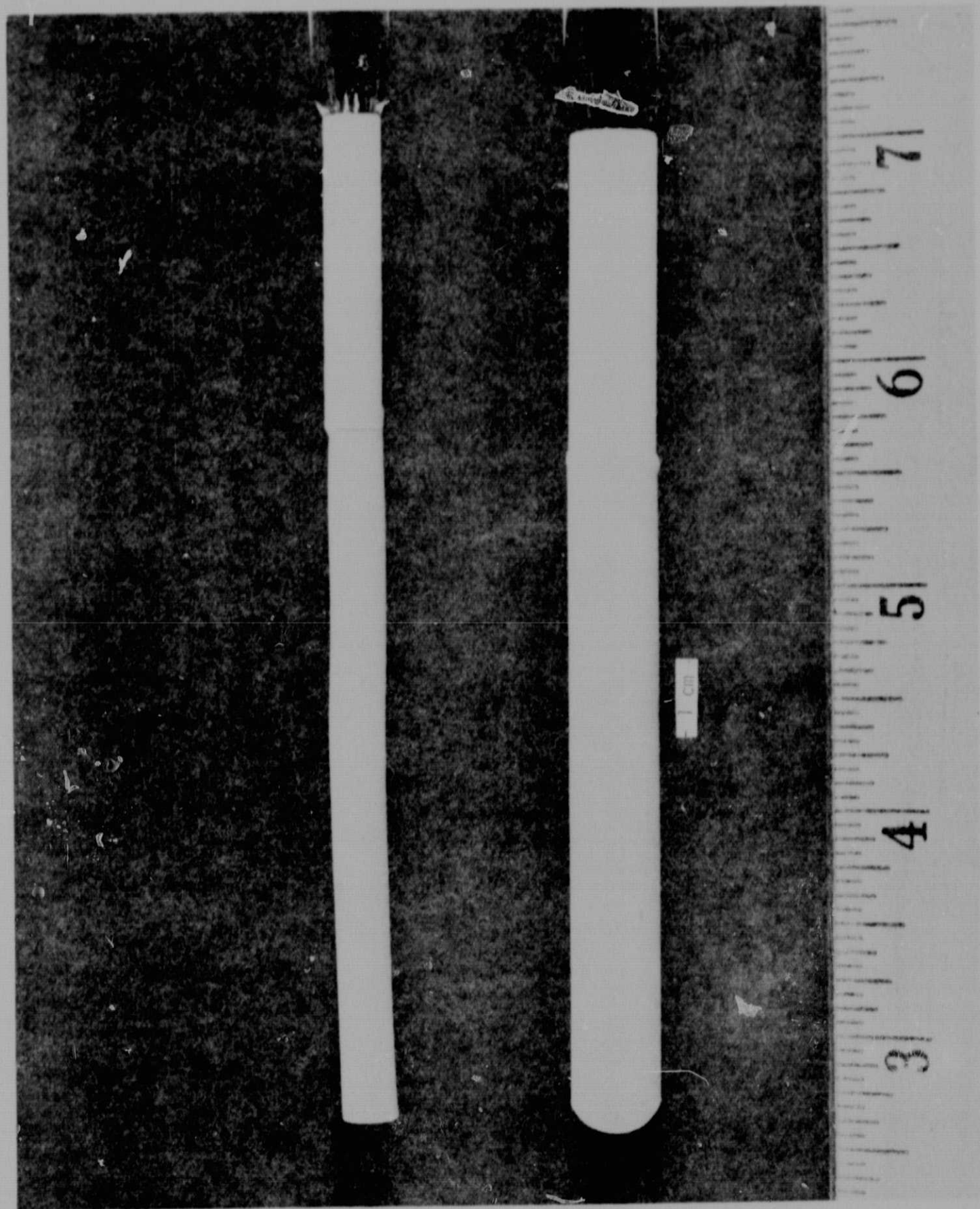


Fig. 16 Sintered β'' -alumina tube, 6 mm O.D. closed with glass, sealed to α - Al_2O_3
and sintered, end-capped β'' -alumina tube, 10 mm O.D., sealed to α - Al_2O_3